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## 煤中硫和汞赋存形态的同步分析 及其相关性研究

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**摘要:**【目的】硫和汞是煤中具有亲和性的两种典型污染元素,明晰煤中硫和汞的赋存形态及其相关性对煤热化学转化过程中含硫含汞污染物的协同治理意义重大。目前,研究者多采用GB/T 215—2003国标法和逐级化学浸提法分别辨析煤中硫和汞的赋存形态,这给深入分析煤中硫含量、汞含量的相关性带来了不便。此外,煤中的细粒黄铁矿不能被HNO<sub>3</sub>有效浸提,意味着国标法会低估含细粒黄铁矿煤中的黄铁矿硫的含量。【方法】基于此,提出了一种更准确的能同步分析煤中硫和汞赋存形态的方法——逐级化学浸提联合等离子体低温灰化法(SCEPs-PLTA),并对40种煤样进行了硫、汞元素的赋存形态分析。【结果】研究表明,与单纯的逐级化学浸提法和国标法相比,SCEPs-PLTA在分析含细粒黄铁矿煤中硫和汞的赋存形态时有显著优势,可将煤中硫化物硫和硫化物结合态汞的含量精度分别最高提升30.37%和24.29%。此外,煤中的硫和汞均以有机(结合)态和硫化物(结合)态为主(两类含量之和占比高于40%),且同种赋存形态的硫和汞含量间具有显著的正相关性。【结论】本研究为煤热化学转化过程中硫和汞的迁移转化及调控奠定了理论基础。

**关键词:**硫;汞;等离子体低温灰化;赋存形态;细粒黄铁矿;相关性

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## Simultaneous Analysis of Sulfur and Mercury Occurrence Forms in Coal and Their Correlation Study

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**Abstract:**【Purposes】Sulfur and mercury are two typical pollutant elements with affinity in coal. Clarifying their occurrence forms and correlation of sulfur and mercury in coal is of great significance

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for the synergistic control of sulfur- and mercury-containing pollutants during coal thermochemical conversion processes. At present, researchers mostly use the national standard method GB/T 215—2003 and sequential chemical extraction method to identify the occurrence forms of sulfur and mercury in coal, respectively, which brings inconvenience to the in-depth analysis of correlation between sulfur content and mercury content in coal. In addition, it is found that fine-grained pyrite in coal cannot be effectively extracted by  $\text{HNO}_3$ , which means that with the national standard method, the content of pyritic sulfur will be under estimated in coal containing fine-grained pyrite. **【Methods】** Thereby, a more accurate method was proposed for the simultaneous analysis of occurrence forms of sulfur and mercury in coal - Sequential Chemical Extraction Procedures Combined with Plasma Low-Temperature Ashing (SCEPs-PLTA). Besides, this proposed method was applied to analyze the occurrence forms of sulfur and mercury elements in 40 coal samples with significant differences in sulfur content, mercury content, and pyrite occurrence form. **【Results】** The research shows that compared with the simple sequential chemical extraction procedures method and the national standard method, SCEPs-PLTA has significant advantages in analyzing the occurrence forms of sulfur and mercury in coal containing fine-grained pyrite, and can improve the measurement accuracy of sulfide sulfur and sulfide-bound mercury contents in coal by up to 30.37% and 24.29%, respectively. In addition, sulfur and mercury in coal are mainly in organic (bound) and sulfide (bound) forms (the sum of the two forms accounts for more than 40%), and there is a significant positive correlation between the contents of sulfur and mercury in the same occurrence form. **【Conclusions】** This study lays a theoretical foundation for the migration, transformation, and regulation of sulfur and mercury in coal thermochemical conversion.

**Keywords:** sulfur; mercury; plasma low-temperature ashing; occurrence form; fine-grained pyrite; correlation

“富煤、贫油、少气”的资源禀赋特点决定了煤炭在我国能源和化工领域具有重要地位。我国煤炭平均硫和汞含量分别为0.04%~9.62%和0.02~1.00  $\mu\text{g/g}$ <sup>[1, 2]</sup>。热化学转化是探索煤炭资源高效清洁利用的有效手段。煤热化学转化过程中释放的含硫化合物会腐蚀设备,使催化剂中毒,污染环境,危害人体健康。硫作为酸雨和酸性矿山废水的主要来源,因其对环境的不良影响而受到广泛关注<sup>[3, 4]</sup>。汞是煤中的微量元素,因其毒性高、迁移距离远、持久性强、生物蓄积性强,对人体和环境有害而备受关注<sup>[1, 5-8]</sup>。

硫和汞是煤中具有亲和性的两种典型污染元素,明晰煤中硫和汞的赋存形态及其相关性对煤热化学转化过程中含硫含汞污染物的协同治理意义重大。煤中的硫主要以无机硫和有机硫的形式存在。无机硫主要是硫化物硫、硫酸盐硫和少量的单质硫。除了黄铁矿硫外,煤中还存在微量的非黄铁矿硫化物,如白铁矿( $\text{FeS}_2$ )、闪锌矿( $\text{ZnS}$ )等<sup>[9, 10]</sup>。硫酸盐可分为可交换性硫酸盐和酸溶性硫酸盐<sup>[11]</sup>,通常在煤中以极微量的形式存在,在氧化煤中,硫酸盐的含量可能会出现局部增加<sup>[12]</sup>。有机硫主要

包含硫醇、硫醚以及含硫杂环(噻吩、硫酮、亚砷和砷)<sup>[13]</sup>。煤中汞的赋存形式具有多样性,其主要以黄铁矿<sup>[14, 15]</sup>、白铁矿<sup>[16]</sup>、有机质<sup>[10, 17, 18]</sup>和单质形式存在。此外,少量汞会选择性地富集于其他硫化物和硒化物矿中,如硒铅矿、硫砷锑矿<sup>[19]</sup>、氯氧汞矿及朱砂<sup>[20]</sup>等矿物相。关于汞在煤中的赋存关系,学术界存在不同的观点:部分研究者认为,汞与黄铁矿在煤基体内以固溶体形式伴生,黄铁矿是单质汞的主要载体矿物<sup>[21-26]</sup>;另有学者提出,煤中有机质的存在与汞含量密切相关<sup>[27]</sup>,推测汞可能与煤基质保护下的细分散黄铁矿存在关联。综合现有研究,煤中汞的赋存形态可进一步细分为单质态、可交换态、氧化物结合态、碳酸盐结合态、硅酸盐结合态、硫化物结合态和有机结合态等类型<sup>[1, 24, 28-33]</sup>。黄铁矿是煤中主要的硫化物矿物,根据粒径可分为易被浸提的粗粒黄铁矿(粒径大于60  $\mu\text{m}$ )<sup>[34, 35]</sup>和不易被浸提的细粒黄铁矿(粒径小于60  $\mu\text{m}$ )<sup>[36-38]</sup>。有研究者认为煤中汞与硫化物有关<sup>[14]</sup>,汞含量与硫含量呈显著正相关性<sup>[39]</sup>,Hg存在很强的亲硫性且与黄铁矿存在密切的伴生关系<sup>[40]</sup>。也有研究者认为煤中汞与灰分、硫酸盐和硫化物含量呈正相关,与有机硫含

量呈负相关<sup>[41]</sup>。还有研究者认为有机硫中的汞含量与硫含量没有相关性<sup>[42]</sup>。关于煤中硫和汞的相关性研究结果不一致,且相同赋存形态硫和汞间的相关性亦不明晰。

根据国家标准 GB/T 215—2003《煤中各种形态硫的测定方法》将煤中不同形态的硫分为:硫酸盐硫、硫化铁硫和有机硫。逐级化学浸提法可以将煤中汞的赋存形态分为:可交换态汞、HCl 可溶态汞、HF 可溶态汞、硫化物结合态汞和有机结合态汞<sup>[43]</sup>。煤中硫和汞赋存形态分析方法的不同为深入分析煤中硫含量、汞含量的相关性带来了不便。此外,煤中的细粒黄铁矿不能被 HNO<sub>3</sub> 有效浸提,意味着国标法会低估含细粒黄铁矿煤中黄铁矿硫的含量。基于此,我们提出了一种更准确的能同步分析煤中硫和汞赋存形态的方法——逐级化学浸提联合等离子体低温灰化法(SCEPs-PLTA),前期的研究<sup>[44]</sup>主要考察了 3 种煤中相同赋存形态硫和汞间的相关性,研究结论不具有普适性,且没有考察粒径对 SCEPs-PLTA 与单纯的逐级化学浸提法间分析偏差的影响,本文系统考察了 40 种不同煤阶、硫含量和汞含量的煤中硫和汞间的相关性,并定量分析了粒径对 SCEPs-PLTA 与单纯的逐级化学浸提法间分析偏差的影响。此研究为煤热化学转化过程硫和汞的迁移转化及定向调控奠定了理论基础。

## 1 实验部分

### 1.1 煤样的选取

本研究选择了产自黑龙江、云南、内蒙古、宁夏、安徽、江苏、河南和澳大利亚等地的 40 种煤阶、硫含量和汞含量不同的煤作为研究对象。分别根据国家标准 GB/T 475—2008、GB/T 474—2008、GB/T 477—2008 进行煤炭的采样、制备和筛分。一次性筛选约 50 g 粒径小于 200 μm 的煤样储存在干燥器中备用。分别根据国家标准 GB/T 212—2008、GB/T 476—2008、GB/T 215—2003 对煤样进行工业分析、元素分析和形态硫分析。采用高频碳硫分析仪(HCS-140)和汞分析仪(Lumex RA915M)的热解附件(PYRO-915+)分别测定煤样中的硫含量和汞含量。40 种煤的工业分析、元素分析、形态硫分析、硫含量和汞含量结果如表 1 所示。由表 1 可知,该批煤样中包括 5 种褐煤、3 种长焰煤、17 种气煤、7 种肥煤、6 种焦煤和 2 种瘦煤。40 种煤的硫含量范围为 0.31%~4.83%,汞含量范围为 44.0~318.5 ng/g。1 号煤的水分含量最高,达

13.24%。3 号和 4 号煤的灰分含量和汞含量最高,灰分含量分别为 73.11% 和 68.43%,汞含量分别为 318.5 ng/g 和 289.4 ng/g。30 号和 31 号煤的硫含量最高,分别为 4.34% 和 4.83%。

### 1.2 煤样的预处理

首先,分别用 MgCl<sub>2</sub>(1 mol/L, 1 g:5 mL)、HCl(质量分数 18%~19%, 1 g:6 mL)、HF(质量分数 40%, 1 g:7.5 mL)浸提煤样。随后,将 HF 浸提后的煤样分别进行 HNO<sub>3</sub>(质量分数 9.3%~9.7%, 1 g:35 mL)浸提和等离子体低温灰化(PLTA)处理。浸提过程为:在 50 °C 下以 500 r/min 的转速搅拌 12 h,浸提完成后经抽滤洗涤至滤液的 pH 值为 7,将滤饼置于鼓风干燥箱内在 60 °C 下干燥 24 h。MgCl<sub>2</sub>、HCl、HF 和 HNO<sub>3</sub> 浸提残渣分别标记为 CoalS1、CoalS2、CoalS3、CoalS4。等离子体低温灰化的过程为:CoalS3 置于等离子体低温灰化仪中,在 60 W 功率下灰化至恒重(每 2 h 进行一次称重,连续 2 次称重的变化≤1%),将低温灰标记为 Coal-SP。逐级化学浸提的浸提收率和等离子体低温灰化的灰余量数据详见表 2。由表 2 可知,3 号和 4 号煤的 HF 的浸提收率明显低于其余煤,说明这两种煤中含有大量的黏土类矿物,灰余量明显高于其余煤,说明两种煤中含有大量的硫化物矿物。

### 1.3 实验方法

图 1 是实验过程流程图示意图,MgCl<sub>2</sub>-HCl-HF-HNO<sub>3</sub>(SCEPs-HNO<sub>3</sub>) 逐步逐级化学浸提和 MgCl<sub>2</sub>-HCl-HF-PLTA(SCEPs-PLTA) 三步逐级化学联合等离子体低温灰化法均可将煤中的硫和汞同步分为可交换态硫和可交换态汞、HCl 可溶态硫和 HCl 可溶态汞、HF 可溶态硫和 HF 可溶态汞、硫化物硫和硫化物结合态汞、有机硫和有机结合态汞 5 种赋存形态。

### 1.4 煤中不同赋存形态硫和汞的计算公式

每一步浸提残渣和等离子体低温灰中硫和汞的标准化含量按照公式(3)和公式(4)计算。

$$\theta_i = \frac{M_i}{M_{i0}} \times 100\% \quad (1)$$

$$\theta_p = \frac{M_p}{M_{p0}} \times 100\% \quad (2)$$

$$S_i = m_i \times \prod_1^i \theta_i \quad (3)$$

$$S_p = m_p \times \prod_1^3 \theta_i \times \theta_p \quad (4)$$

式中  $\theta_i$  是第  $i$  步的浸提收率,  $M_i$  和  $M_{i0}$  分别为第  $i$  步

表 1 40 种煤的工业分析、元素分析、形态硫分析、硫含量和汞含量  
Table 1 Proximate analysis, ultimate analysis, sulfur forms analysis, sulfur content, and mercury content of 40 kinds of coal

| 煤样 | 工业分析/%      |          |              | 元素分析(daf)/% |        |        |        |          | 形态硫(ad)/% |          |          |            | $w(S)/\%$ | $x(Hg)/(ng\cdot g^{-1})$ |
|----|-------------|----------|--------------|-------------|--------|--------|--------|----------|-----------|----------|----------|------------|-----------|--------------------------|
|    | $w(M_{ad})$ | $w(A_d)$ | $w(V_{daf})$ | $w(C)$      | $w(H)$ | $w(N)$ | $w(S)$ | $w(O^*)$ | $w(S_f)$  | $w(S_s)$ | $w(S_p)$ | $w(S_o^*)$ |           |                          |
| 1  | 13.24       | 19.85    | 62.15        | 67.44       | 9.20   | 1.29   | 0.23   | 21.84    | 0.16      | 0.00     | 0.02     | 0.14       | 0.31      | 72.8                     |
| 2  | 6.70        | 6.90     | 56.10        | 68.31       | 10.39  | 2.36   | 1.50   | 17.44    | 1.30      | 0.06     | 0.06     | 1.18       | 1.35      | 115.4                    |
| 3  | 0.42        | 73.11    | 46.38        | 61.69       | 5.53   | 1.16   | 7.13   | 24.49    | 1.91      | 0.02     | 1.52     | 0.37       | 2.00      | 318.5                    |
| 4  | 0.37        | 68.43    | 42.16        | 66.23       | 5.28   | 1.14   | 5.66   | 21.69    | 1.78      | 0.02     | 1.39     | 0.37       | 1.85      | 289.4                    |
| 5  | 1.16        | 13.48    | 41.18        | 82.18       | 5.43   | 1.47   | 3.51   | 7.41     | 3.00      | 0.14     | 1.19     | 1.67       | 3.50      | 85.3                     |
| 6  | 2.60        | 23.81    | 39.21        | 79.56       | 4.76   | 0.98   | 3.25   | 11.45    | 2.41      | 0.91     | 1.09     | 0.41       | 2.38      | 155.5                    |
| 7  | 1.30        | 10.33    | 37.88        | 82.01       | 5.15   | 1.47   | 0.71   | 10.66    | 0.63      | 0.05     | 0.11     | 0.47       | 0.94      | 88.0                     |
| 8  | 1.42        | 23.52    | 37.64        | 81.19       | 4.79   | 2.02   | 1.94   | 10.06    | 1.46      | 0.20     | 0.42     | 0.84       | 1.68      | 88.4                     |
| 9  | 1.06        | 9.32     | 36.78        | 78.69       | 4.75   | 1.34   | 0.85   | 14.37    | 0.76      | 0.04     | 0.19     | 0.53       | 1.05      | 106.0                    |
| 10 | 1.10        | 9.06     | 36.62        | 84.03       | 5.14   | 1.53   | 0.86   | 8.44     | 0.77      | 0.04     | 0.16     | 0.57       | 1.07      | 90.7                     |
| 11 | 1.22        | 10.68    | 36.42        | 82.94       | 5.22   | 1.34   | 0.95   | 9.55     | 0.84      | 0.04     | 0.14     | 0.66       | 1.10      | 54.9                     |
| 12 | 1.15        | 9.91     | 36.09        | 83.07       | 5.22   | 1.34   | 0.89   | 9.48     | 0.79      | 0.04     | 0.10     | 0.65       | 1.07      | 55.3                     |
| 13 | 3.80        | 13.99    | 35.92        | 80.87       | 6.74   | 1.55   | 2.79   | 8.05     | 2.31      | 0.32     | 0.76     | 1.23       | 2.49      | 120.8                    |
| 14 | 9.38        | 25.42    | 34.09        | 79.20       | 4.19   | 0.81   | 1.95   | 13.85    | 1.32      | 0.19     | 0.66     | 0.47       | 1.53      | 60.6                     |
| 15 | 0.88        | 13.73    | 33.87        | 85.88       | 5.20   | 1.47   | 2.00   | 5.45     | 1.71      | 0.16     | 0.69     | 0.86       | 2.06      | 91.8                     |
| 16 | 1.40        | 12.98    | 33.55        | 82.21       | 4.90   | 1.40   | 1.93   | 9.56     | 1.66      | 0.09     | 0.19     | 1.38       | 1.98      | 170.3                    |
| 17 | 1.31        | 8.54     | 33.26        | 83.85       | 4.89   | 1.09   | 0.91   | 9.26     | 0.82      | 0.12     | 0.20     | 0.50       | 1.10      | 107.8                    |
| 18 | 4.26        | 9.89     | 32.97        | 80.43       | 4.43   | 1.36   | 0.53   | 13.25    | 0.46      | 0.04     | 0.06     | 0.36       | 0.69      | 115.9                    |
| 19 | 0.90        | 15.09    | 32.62        | 85.68       | 5.16   | 1.30   | 0.93   | 6.93     | 0.78      | 0.05     | 0.09     | 0.64       | 1.03      | 44.0                     |
| 20 | 0.72        | 10.07    | 32.38        | 85.91       | 5.15   | 1.47   | 1.68   | 5.79     | 1.50      | 0.06     | 0.20     | 1.24       | 1.89      | 55.3                     |
| 21 | 1.70        | 18.15    | 31.71        | 81.33       | 4.90   | 1.37   | 2.51   | 9.89     | 2.02      | 0.82     | 0.15     | 1.05       | 2.44      | 176.5                    |
| 22 | 1.05        | 9.82     | 31.56        | 89.34       | 7.44   | 2.24   | 0.38   | 0.60     | 0.34      | 0.00     | 0.05     | 0.29       | 0.53      | 159.4                    |
| 23 | 1.35        | 14.29    | 31.53        | 83.51       | 5.01   | 1.44   | 2.20   | 7.84     | 1.86      | 0.68     | 0.18     | 1.00       | 2.21      | 172.0                    |
| 24 | 1.08        | 10.96    | 31.27        | 86.76       | 7.25   | 2.17   | 0.48   | 3.34     | 0.42      | 0.00     | 0.06     | 0.36       | 0.61      | 156.1                    |
| 25 | 0.65        | 11.22    | 30.59        | 86.34       | 5.09   | 1.33   | 0.99   | 6.25     | 0.87      | 0.05     | 0.15     | 0.67       | 1.12      | 184.0                    |
| 26 | 0.76        | 12.45    | 29.82        | 87.45       | 5.04   | 1.70   | 0.84   | 4.97     | 0.73      | 0.05     | 0.15     | 0.53       | 0.99      | 56.3                     |
| 27 | 0.56        | 9.63     | 29.32        | 86.87       | 5.06   | 1.38   | 2.03   | 4.66     | 1.82      | 0.07     | 0.43     | 1.32       | 2.25      | 75.9                     |
| 28 | 0.45        | 11.29    | 29.06        | 86.80       | 5.02   | 1.45   | 2.15   | 4.58     | 1.90      | 0.08     | 0.27     | 1.55       | 2.25      | 107.5                    |
| 29 | 0.34        | 10.30    | 28.59        | 86.73       | 4.97   | 1.43   | 2.24   | 4.63     | 2.00      | 0.10     | 0.37     | 1.53       | 2.45      | 103.1                    |
| 30 | 0.44        | 8.78     | 27.56        | 85.95       | 4.89   | 1.26   | 4.32   | 3.58     | 3.92      | 0.07     | 0.19     | 3.66       | 4.34      | 100.7                    |
| 31 | 0.25        | 8.85     | 26.84        | 86.21       | 4.81   | 1.20   | 4.80   | 2.98     | 4.36      | 0.03     | 0.19     | 4.14       | 4.83      | 102.0                    |
| 32 | 0.80        | 7.13     | 26.40        | 85.84       | 5.10   | 1.78   | 1.63   | 5.65     | 1.50      | 0.55     | 0.11     | 0.84       | 1.84      | 56.4                     |
| 33 | 0.80        | 10.54    | 24.48        | 88.73       | 6.37   | 2.01   | 0.63   | 2.26     | 0.56      | 0.02     | 0.14     | 0.40       | 0.77      | 164.9                    |
| 34 | 1.54        | 10.18    | 22.22        | 88.69       | 5.96   | 2.57   | 0.63   | 2.15     | 0.56      | 0.04     | 0.04     | 0.48       | 0.77      | 62.3                     |
| 35 | 1.60        | 13.92    | 21.30        | 86.68       | 4.53   | 1.46   | 2.36   | 4.97     | 2.00      | 1.02     | 0.15     | 0.83       | 2.32      | 125.3                    |
| 36 | 0.39        | 16.16    | 21.22        | 88.43       | 4.69   | 1.53   | 0.95   | 4.40     | 0.79      | 0.03     | 0.23     | 0.53       | 1.01      | 48.0                     |
| 37 | 0.52        | 10.05    | 21.21        | 87.81       | 4.58   | 1.30   | 2.73   | 3.58     | 2.44      | 0.07     | 0.14     | 2.23       | 2.82      | 63.1                     |
| 38 | 0.50        | 12.38    | 19.05        | 87.76       | 4.44   | 1.31   | 2.73   | 3.76     | 2.38      | 0.05     | 0.24     | 2.09       | 2.77      | 54.2                     |
| 39 | 1.09        | 11.33    | 17.45        | 90.10       | 5.23   | 2.01   | 0.50   | 2.16     | 0.44      | 0.04     | 0.08     | 0.32       | 0.63      | 70.2                     |
| 40 | 0.54        | 15.25    | 16.34        | 89.67       | 4.39   | 1.52   | 0.97   | 3.45     | 0.82      | 0.03     | 0.38     | 0.41       | 1.13      | 126.9                    |

注:1-5是褐煤;6-8是长焰煤;9-25是气煤;26-32是肥煤;33-38是焦煤;39和40是瘦煤;\*通过差减计算

浸提后和浸提前样品的质量,  $\theta_p$  是等离子体低温灰化的灰余量,  $M_p$  和  $M_{p0}$  分别为等离子体低温灰化后和灰化前样品的质量,  $S_i$  是第  $i$  步浸提残渣中硫或汞的标准化含量,  $m_i$  是第  $i$  步浸提残渣中硫或汞的检测含量,  $S_p$  是等离子体低温灰中硫或汞的标准化含量,  $m_p$  是等离子体低温灰中硫或汞的检测含量。

煤中不同赋存形态的硫和汞含量按照公式(5)一公式(9),通过逐级差减计算。

表 2 SCEPs 的浸提收率和 PLTA 的灰余量  
Table 2 Extraction rate of SCEPs and ash allowance of PLTA

| 煤样 | 浸提收率/% |        |        |        |        | 煤样 | 浸提收率/% |        |        |        |        |
|----|--------|--------|--------|--------|--------|----|--------|--------|--------|--------|--------|
|    | CoalS1 | CoalS2 | CoalS3 | CoalS4 | CoalSP |    | CoalS1 | CoalS2 | CoalS3 | CoalS4 | CoalSP |
| 1  | 96.30  | 91.44  | 78.88  | 99.25  | 1.12   | 21 | 93.90  | 97.00  | 80.33  | 99.93  | 1.56   |
| 2  | 95.50  | 92.11  | 93.75  | 99.97  | 1.16   | 22 | 98.20  | 98.33  | 85.25  | 99.95  | 1.15   |
| 3  | 97.90  | 90.13  | 21.33  | 77.00  | 15.23  | 23 | 94.70  | 98.63  | 83.83  | 99.99  | 1.84   |
| 4  | 99.00  | 93.38  | 28.17  | 85.00  | 13.92  | 24 | 97.60  | 97.89  | 88.75  | 99.94  | 1.16   |
| 5  | 97.60  | 97.88  | 87.67  | 99.95  | 11.97  | 25 | 98.90  | 99.88  | 77.33  | 99.95  | 1.52   |
| 6  | 97.54  | 92.76  | 87.72  | 99.35  | 2.18   | 26 | 98.30  | 96.50  | 86.00  | 99.89  | 1.53   |
| 7  | 97.90  | 97.63  | 90.17  | 98.00  | 1.12   | 27 | 98.70  | 98.63  | 87.33  | 99.88  | 4.32   |
| 8  | 94.80  | 86.75  | 81.33  | 98.25  | 4.23   | 28 | 97.70  | 99.88  | 88.17  | 99.91  | 2.75   |
| 9  | 97.50  | 98.00  | 89.33  | 99.98  | 1.93   | 29 | 97.50  | 98.00  | 87.50  | 99.92  | 3.75   |
| 10 | 98.90  | 96.63  | 92.50  | 98.00  | 1.68   | 30 | 98.20  | 98.25  | 89.33  | 99.93  | 1.95   |
| 11 | 98.00  | 98.13  | 90.00  | 99.89  | 1.42   | 31 | 98.30  | 98.50  | 89.00  | 99.00  | 1.95   |
| 12 | 96.80  | 99.88  | 87.00  | 98.00  | 0.95   | 32 | 96.70  | 97.50  | 93.83  | 99.75  | 1.17   |
| 13 | 93.60  | 95.67  | 87.63  | 99.24  | 1.86   | 33 | 98.10  | 98.89  | 88.75  | 99.86  | 1.24   |
| 14 | 92.50  | 93.21  | 77.93  | 99.33  | 2.03   | 34 | 98.30  | 99.96  | 86.05  | 99.96  | 1.14   |
| 15 | 97.40  | 97.00  | 86.33  | 99.55  | 6.63   | 35 | 91.30  | 98.50  | 88.17  | 98.50  | 1.55   |
| 16 | 99.50  | 97.88  | 84.50  | 98.50  | 1.98   | 36 | 98.90  | 99.38  | 80.67  | 99.92  | 2.31   |
| 17 | 97.00  | 94.88  | 93.50  | 99.93  | 2.01   | 37 | 99.00  | 97.50  | 87.83  | 99.93  | 1.41   |
| 18 | 98.00  | 96.58  | 92.33  | 99.82  | 1.61   | 38 | 98.10  | 98.25  | 85.33  | 99.89  | 2.41   |
| 19 | 97.70  | 97.88  | 83.50  | 99.99  | 0.97   | 39 | 96.70  | 97.33  | 88.30  | 99.92  | 1.18   |
| 20 | 98.40  | 99.50  | 89.33  | 99.89  | 2.05   | 40 | 99.10  | 98.75  | 82.67  | 99.00  | 3.85   |

注:1-5 是褐煤;6-8 是长焰煤;9-25 是气煤;26-32 是肥煤;33-38 是焦煤;39 和 40 是瘦煤

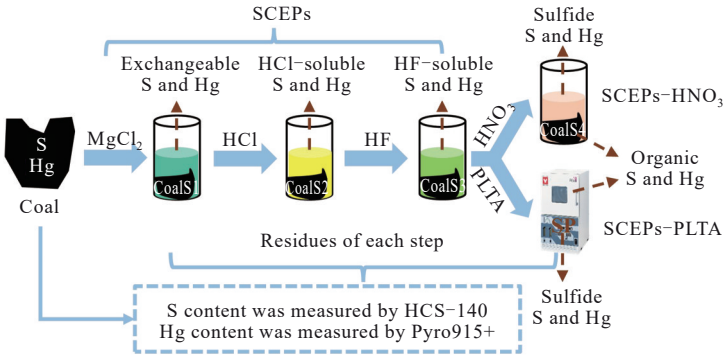


图 1 实验过程流程示意图  
Fig.1 Schematic diagram of the experimental processes

可交换态硫或汞= $S_0-S_1$ . (5)

HCl 可溶态硫或汞= $S_1-S_2$ . (6)

HF 可溶态硫或汞= $S_2-S_3$ . (7)

硫化物硫或硫化物结合态汞= $S_3-S_4=S_p$ . (8)

有机硫或有机结合态汞= $S_4-S_3-S_p$ . (9)

准 GB/T 16773—2008《煤岩分析样品制备方法》制备粉煤光片)中黄铁矿的赋存形态进行鉴定和拍摄,原煤和脱矿煤中黄铁矿的微观赋存形态结果分别如图 2 和图 3 所示。由图 2 可知,3、4、6、13 和 32 号煤中主要含粗粒黄铁矿;1、2、7、9、10、11、12、15、18、22、31、33、35、36、37、39 和 40 号煤中主要含细粒黄铁矿;5、8、14、16、17、19、20、21、23、24、25、26、27、28、29、30、34、38 号煤中同时含粗粒黄铁矿和细粒黄铁矿。40 种煤中仅含粗粒黄铁矿的煤占 12.5%,其余 87.5% 的煤中均含细粒黄铁矿。由图 3 可知,3S4、4S4、6S4、13S4 和 32S4 中无黄铁矿,其余 HNO<sub>3</sub>

2 结果与讨论

2.1 原煤和脱矿煤中黄铁矿的赋存形态

煤样中黄铁矿的赋存形态由光学显微镜(OM, Laica, DMC-4500)检测。在反射光条件下,使用徕卡 DMC-4500 光学显微镜对粉煤光片(根据国家标

浸提后煤样中均含细粒黄铁矿。结合前期研究<sup>[44]</sup>进

一步说明  $\text{HNO}_3$  不能完全浸提煤中的细粒黄铁矿。

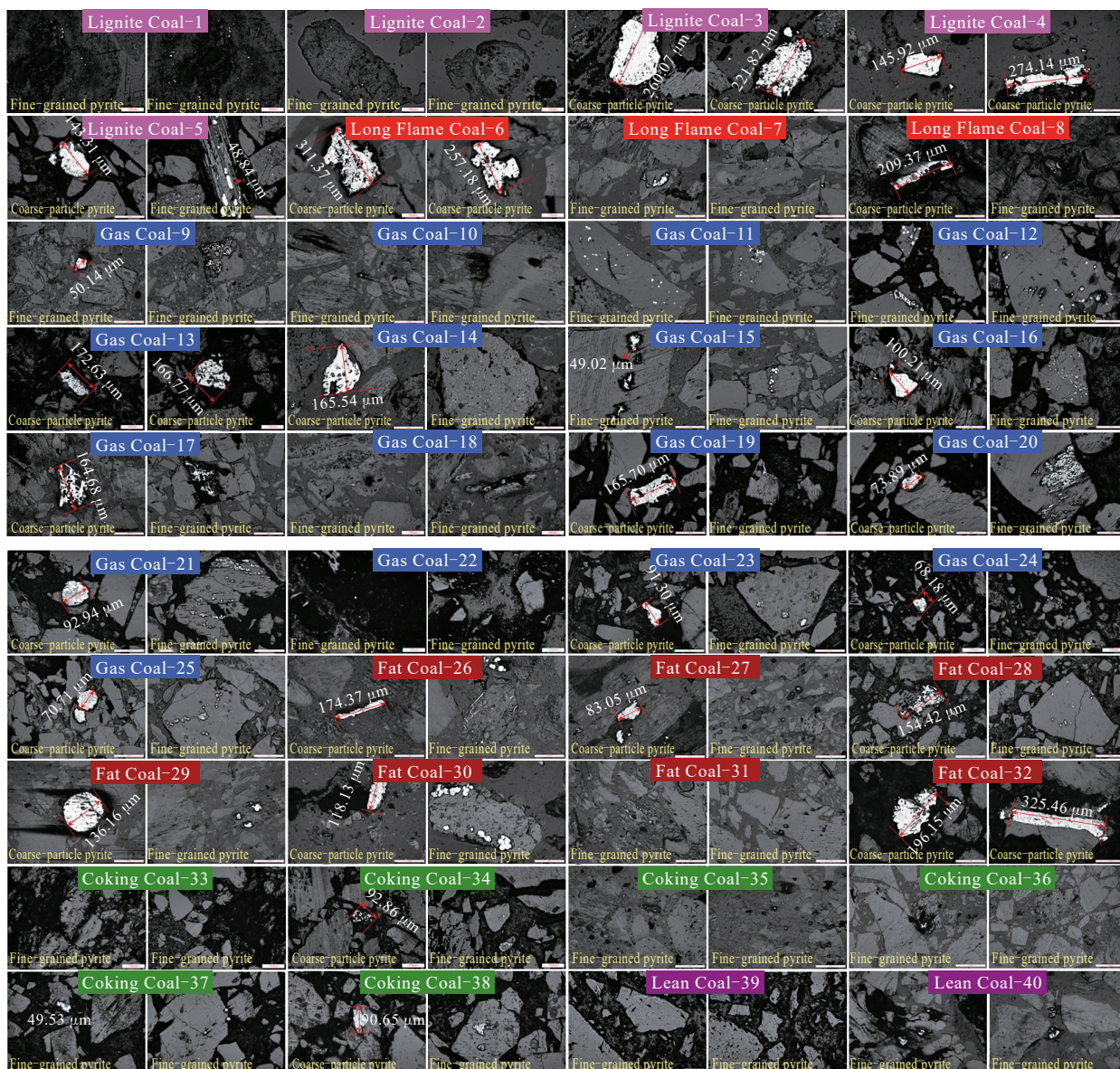


图2 原煤中黄铁矿的微观赋存形态

Fig.2 Microscopic occurrence forms of pyrite in raw coal

## 2.2 不同方法测得煤中硫和汞赋存形态的对比分析

### 2.2.1 SCEPs-PLTA 与国标法对比分析

将 SCEPs-PLTA 测得的  $\text{HCl}$  可溶态硫、硫化物硫和有机硫进行归一化后分别与国标法测得的  $S_s$ 、 $S_p$  和  $S_o$  进行对比分析,结果如表 3 和图 4 所示。因为国标法测得的  $S_s$  中同时包含了可交换性硫酸盐和酸溶性硫酸盐,所以  $S_s$  含量较  $\text{HCl}$  可溶态硫的含量偏高。煤中含有多种多样的硫化物,包括含铁元素的黄铁矿、磁铁矿和黄铜矿以及不含铁元素的闪锌矿和方铅矿,而国标法只能检测含有铁元素的硫化物,故硫化物硫的含量高于  $S_p$ 。此外,因 1、2、

5、7—12、14—31、33—40 号煤中含有用  $\text{HNO}_3$  难以浸提的细粒黄铁矿,也可导致这 35 种煤中  $S_p$  的检测值较硫化硫含量偏低,  $S_o$  的检测值较有机硫含量偏高。这与煤中非黄铁矿的存在使得硫化物硫含量被低估的结论一致<sup>[10,12]</sup>。根据以上分析可知,国标法会将不含铁的硫化物硫、 $\text{HNO}_3$  不易浸提的细粒黄铁矿硫和  $\text{HF}$  可溶态硫归类到  $S_o$  中;可交换态硫归类到  $S_s$  中。相比国标法, SCEPs-PLTA 可将煤中的硫细分为 5 种赋存形态,且能够避免煤中细粒黄铁矿的影响。

### 2.2.2 SCEPs-PLTA 与 SCEPs- $\text{HNO}_3$ 对比分析

相比 SCEPs- $\text{HNO}_3$  法, SCEPs-PLTA 测得的

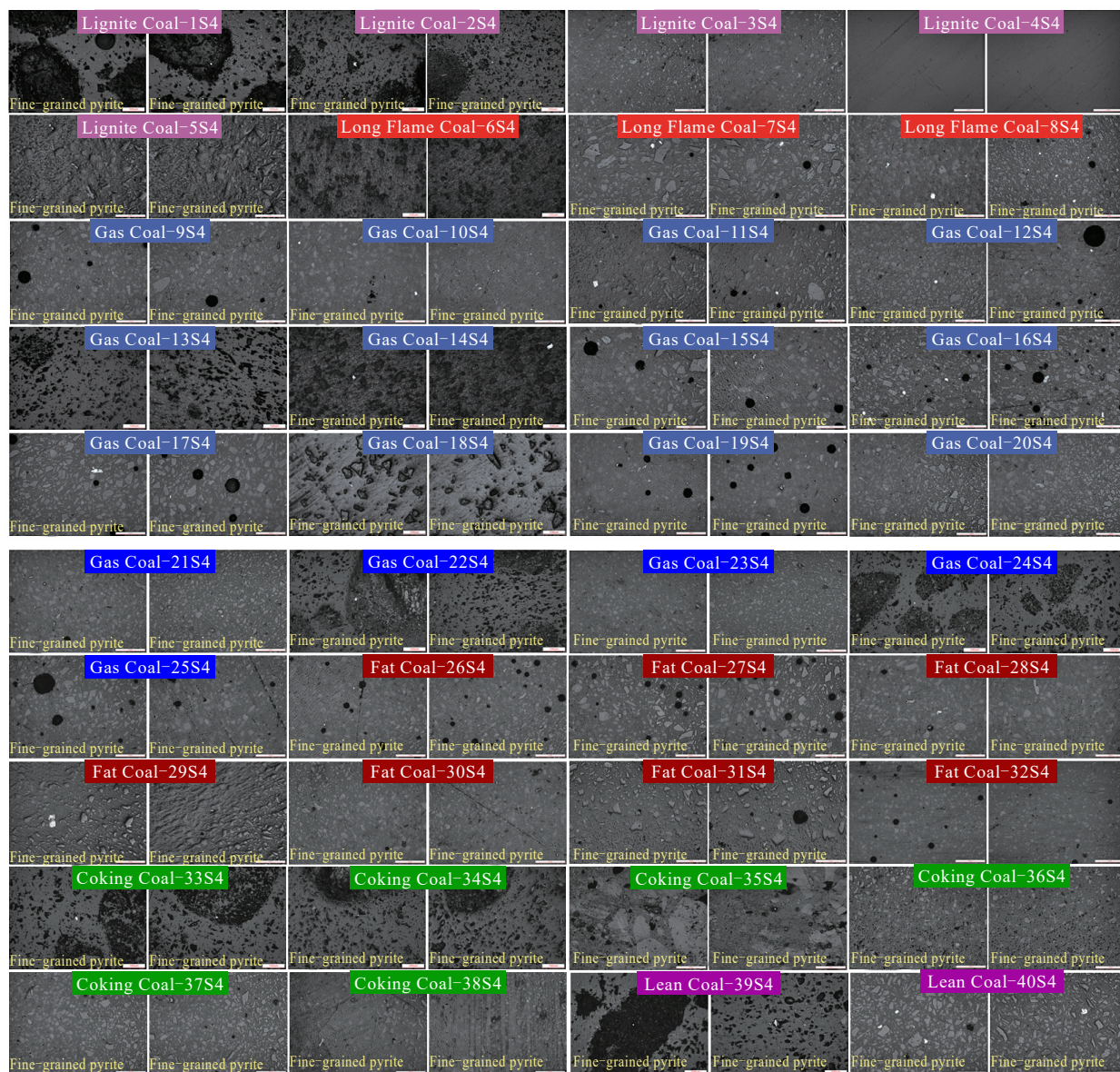


图 3 脱矿煤中黄铁矿的微观赋存形态

Fig.3 Microscopic occurrence forms of pyrite in demineralized coal

硫化物硫和硫化物结合态汞含量偏高,有机硫和有机结合态汞含量偏低(见表 4 和图 5)。主要是  $\text{HNO}_3$  浸提不完全煤中的细粒黄铁矿,使得这部分细粒黄铁矿硫和汞归类到了有机硫和有机结合态汞所致。这与不易被  $\text{HNO}_3$  浸提的细粒黄铁矿会使得有机硫和有机结合态汞的含量被高估的结论一致<sup>[1, 12]</sup>。由表 4 中 SCEPs-PLTA 和 SCEPs- $\text{HNO}_3$  法分析煤中有机硫(硫化物硫)的占比偏差绝对值数据可知,3、4、6、13 和 32 号煤中主要含粗粒黄铁矿, SCEPs-PLTA 与 SCEPs- $\text{HNO}_3$  法检测结果偏差为 0.11%~0.97%;2 号煤中硫含量高且主要含细粒黄铁矿,两种方法检测结果偏差较大,达 30.37%;其余煤采用两种方法检测结果偏差在

1.87%~13.44% 范围内。

由表 4 中 SCEPs-PLTA 和 SCEPs- $\text{HNO}_3$  法分析煤中有机结合态汞(硫化物结合态汞)的占比偏差绝对值数据可知,3、4、6、13 和 32 号煤中主要含粗粒黄铁矿, SCEPs-PLTA 与 SCEPs- $\text{HNO}_3$  法检测结果偏差小于 0.24%~0.65%;2 号煤中硫含量高且主要含细粒黄铁矿,两种方法检测结果偏差较大,达 24.29%;其余煤采用两种方法检测结果偏差在 1.68%~13.21% 范围内。两种方法的分析偏差取决于煤中细粒黄铁矿的含量以及细粒黄铁矿中伴生的汞含量。相比 SCEPs- $\text{HNO}_3$ , SCEPs-PLTA 在同步分析含细粒黄铁矿煤中硫和汞的赋存形态方面具有显著优势。

表 3 国标法和 SCEPs-PLTA 法测得的形态硫含量数据  
Table 3 Sulfur forms and contents measured by national standard and SCEPs-PLTA methods

| 煤样 | <sup>a</sup> 形态硫百分比/% |                |                             | <sup>b</sup> 形态硫百分比/% |           |           | 煤样 | <sup>a</sup> 形态硫百分比/% |                |                             | <sup>b</sup> 形态硫百分比/% |           |           |
|----|-----------------------|----------------|-----------------------------|-----------------------|-----------|-----------|----|-----------------------|----------------|-----------------------------|-----------------------|-----------|-----------|
|    | S <sub>s</sub>        | S <sub>p</sub> | S <sub>o</sub> <sup>*</sup> | HCl-soluble S         | Sulfide S | Organic S |    | S <sub>s</sub>        | S <sub>p</sub> | S <sub>o</sub> <sup>*</sup> | HCl-soluble S         | Sulfide S | Organic S |
| 1  | 0.00                  | 12.50          | 87.50                       | 0.00                  | 22.58     | 77.42     | 21 | 40.59                 | 7.43           | 51.98                       | 4.69                  | 44.53     | 50.78     |
| 2  | 4.62                  | 4.62           | 90.77                       | 0.76                  | 37.88     | 61.36     | 22 | 0.00                  | 14.71          | 85.29                       | 0.00                  | 29.41     | 70.59     |
| 3  | 1.05                  | 79.58          | 19.37                       | 0.51                  | 80.71     | 18.78     | 23 | 36.56                 | 9.68           | 53.76                       | 6.47                  | 41.01     | 52.52     |
| 4  | 1.12                  | 78.09          | 20.79                       | 0.55                  | 79.56     | 19.89     | 24 | 0.00                  | 14.29          | 85.71                       | 0.00                  | 27.87     | 72.13     |
| 5  | 4.67                  | 39.67          | 55.67                       | 1.00                  | 49.83     | 49.16     | 25 | 5.75                  | 17.24          | 77.01                       | 5.05                  | 21.21     | 73.74     |
| 6  | 37.76                 | 45.23          | 17.01                       | 36.62                 | 46.48     | 16.90     | 26 | 6.85                  | 20.55          | 72.60                       | 1.16                  | 33.72     | 65.12     |
| 7  | 7.94                  | 17.46          | 74.60                       | 3.37                  | 25.84     | 70.79     | 27 | 3.85                  | 23.63          | 72.53                       | 2.40                  | 36.06     | 61.54     |
| 8  | 13.70                 | 28.77          | 57.53                       | 1.74                  | 42.61     | 55.65     | 28 | 4.21                  | 14.21          | 81.58                       | 3.81                  | 20.48     | 75.71     |
| 9  | 5.26                  | 25.00          | 69.74                       | 1.98                  | 39.60     | 58.42     | 29 | 5.00                  | 18.50          | 76.50                       | 2.97                  | 24.58     | 72.46     |
| 10 | 5.19                  | 20.78          | 74.03                       | 1.04                  | 26.04     | 72.92     | 30 | 1.79                  | 4.85           | 93.37                       | 0.77                  | 11.73     | 87.50     |
| 11 | 4.76                  | 16.67          | 78.57                       | 0.94                  | 25.47     | 73.58     | 31 | 0.69                  | 4.36           | 94.95                       | 0.68                  | 9.50      | 89.82     |
| 12 | 5.06                  | 12.66          | 82.28                       | 1.94                  | 17.48     | 80.58     | 32 | 36.67                 | 7.33           | 56.00                       | 8.33                  | 41.67     | 50.00     |
| 13 | 13.85                 | 32.90          | 53.25                       | 4.74                  | 43.68     | 51.58     | 33 | 3.57                  | 25.00          | 71.43                       | 1.35                  | 35.14     | 63.51     |
| 14 | 14.39                 | 50.00          | 35.61                       | 12.88                 | 56.06     | 31.06     | 34 | 7.14                  | 7.14           | 85.71                       | 2.86                  | 15.71     | 81.43     |
| 15 | 9.36                  | 40.35          | 50.29                       | 0.56                  | 50.56     | 48.88     | 35 | 51.00                 | 7.50           | 41.50                       | 1.80                  | 57.66     | 40.54     |
| 16 | 5.42                  | 11.45          | 83.13                       | 4.71                  | 12.57     | 82.72     | 36 | 3.80                  | 29.11          | 67.09                       | 2.02                  | 37.37     | 60.61     |
| 17 | 14.63                 | 24.39          | 60.98                       | 5.15                  | 35.05     | 59.79     | 37 | 2.87                  | 5.74           | 91.39                       | 2.70                  | 11.20     | 86.10     |
| 18 | 8.70                  | 13.04          | 78.26                       | 6.35                  | 20.63     | 73.02     | 38 | 2.10                  | 10.08          | 87.82                       | 2.00                  | 14.00     | 84.00     |
| 19 | 6.41                  | 11.54          | 82.05                       | 0.00                  | 29.90     | 70.10     | 39 | 9.09                  | 18.18          | 72.73                       | 3.57                  | 25.00     | 71.43     |
| 20 | 4.00                  | 13.33          | 82.67                       | 0.00                  | 21.02     | 78.98     | 40 | 3.66                  | 46.34          | 50.00                       | 1.00                  | 54.00     | 45.00     |

注:<sup>a</sup>是国标法的分析结果;<sup>b</sup>是 SCEPs-PLTA 法的分析结果;\*通过差减计算

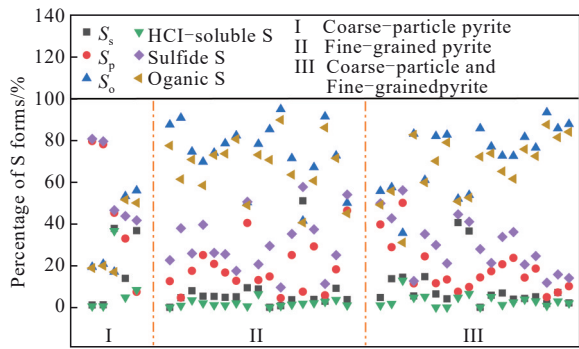


图 4 国标法和 SCEPs-PLTA 测得的形态硫结果  
Fig.4 Sulfur forms measured by national standard and SCEPs-PLTA methods

### 2.2.3 煤样粒径对 SCEPs-PLTA 和 SCEPs-HNO<sub>3</sub> 法分析偏差的影响

选取脱矿煤在 OM 下黄铁矿分布较多的粒径小于 200  $\mu\text{m}$  的 8 号、11 号、12 号、14 号、16 号和 40 号 6 种样继续研磨,过 500 目筛,制备粒径小于 30  $\mu\text{m}$  的煤样。采用 SCEPs-HNO<sub>3</sub> 和 SCEPs-PLTA 法同步分析上述 6 种煤样中硫和汞的赋存形态,并与粒径小于 200  $\mu\text{m}$  的煤样对比分析粒径对两种方法偏差的影响,结果如表 5 所示。粒径小于 200  $\mu\text{m}$  的煤样采用两种方法分析得到的硫和汞含量偏差绝对值

分别为 5.26%~12.12% 和 4.17%~12.93%。而粒径小于 30  $\mu\text{m}$  的煤样两种方法分析得到的硫和汞含量偏差绝对值分别为 1.46%~7.55% 和 1.08%~8.05%。说明,减小煤样粒径至 30  $\mu\text{m}$  可减小两种方法间的偏差,分别减小了 3.8%~4.57% 和 3.09%~4.88%。同时,将粒径小于 30  $\mu\text{m}$  煤样的脱矿煤制备粉煤光片,在 OM 下观察黄铁矿的微观赋存形态,结果如图 6 所示,发现脱矿煤中均有细粒黄铁矿存在。进一步说明,虽然减小煤样粒径至 30  $\mu\text{m}$  可显著减小由细粒黄铁矿带来的 SCEPs-HNO<sub>3</sub> 和 SCEPs-PLTA 法间的偏差,但煤中的细粒黄铁矿用 HNO<sub>3</sub> 依然无法完全浸提。SCEPs-PLTA 法在分析含细粒黄铁矿煤中硫和汞的赋存形态方面有明显的优势。

### 2.3 SCEPs-PLTA 同步分析煤中硫和汞的赋存形态

采用 SCEPs-PLTA 法同步分析 40 种煤中硫和汞的赋存形态,结果如表 6 所示。40 种煤中有 30% 的煤以有机硫为主(占比超 70%),5% 的煤以硫化物硫为主,42.5% 的煤以有机硫和硫化物硫为主(二者占比之和超 80%),17.5% 的煤以有机硫、硫

表 4 SCEPs-HNO<sub>3</sub>和 SCEPs-PLTA 法测得煤中不同赋存形态硫和汞含量数据  
Table 4 Contents of different forms of sulfur and mercury in coal measured by SCEPs-HNO<sub>3</sub> and SCEPs-PLTA methods

| 煤样 | 元素 | 形态硫和形态汞的百分占比/% |       |      |                 |                |                 |                | 差值    | 煤样 | 元素 | 形态硫和形态汞的百分占比/% |       |       |                 |                |                 |                | 差值    |
|----|----|----------------|-------|------|-----------------|----------------|-----------------|----------------|-------|----|----|----------------|-------|-------|-----------------|----------------|-----------------|----------------|-------|
|    |    | I              | II    | III  | <sup>a</sup> IV | <sup>a</sup> V | <sup>b</sup> IV | <sup>b</sup> V |       |    |    | I              | II    | III   | <sup>a</sup> IV | <sup>a</sup> V | <sup>b</sup> IV | <sup>b</sup> V |       |
| 1  | S  | 0.00           | 0.00  | 0.00 | 12.90           | 87.10          | 22.58           | 77.42          | 9.68  | 21 | S  | 38.52          | 2.46  | 9.02  | 12.61           | 37.39          | 23.36           | 26.64          | 10.75 |
|    | Hg | 0.78           | 0.52  | 0.71 | 14.64           | 83.35          | 20.33           | 77.66          | 5.69  |    | Hg | 1.21           | 35.78 | 5.76  | 14.38           | 42.87          | 24.90           | 32.35          | 10.52 |
| 2  | S  | 1.48           | 0.74  | 0.74 | 6.67            | 90.37          | 37.04           | 60.00          | 30.37 | 22 | S  | 0.00           | 0.00  | 3.77  | 15.09           | 81.14          | 28.30           | 67.93          | 13.21 |
|    | Hg | 5.57           | 3.11  | 3.85 | 7.24            | 80.23          | 31.53           | 55.94          | 24.29 |    | Hg | 0.75           | 0.45  | 3.21  | 17.40           | 78.19          | 27.72           | 67.87          | 10.32 |
| 3  | S  | 1.00           | 0.50  | 0.50 | 79.39           | 18.61          | 79.50           | 18.50          | 0.11  | 23 | S  | 33.03          | 4.07  | 4.07  | 13.06           | 45.77          | 25.79           | 33.04          | 12.73 |
|    | Hg | 0.87           | 7.96  | 1.83 | 70.51           | 18.83          | 70.78           | 18.56          | 0.27  |    | Hg | 16.42          | 13.63 | 2.52  | 19.26           | 48.17          | 30.32           | 37.11          | 11.06 |
| 4  | S  | 2.16           | 0.54  | 0.00 | 76.87           | 20.43          | 77.84           | 19.46          | 0.97  | 24 | S  | 0.00           | 0.00  | 0.00  | 16.39           | 83.61          | 27.87           | 72.13          | 11.48 |
|    | Hg | 1.82           | 1.49  | 2.57 | 71.01           | 23.11          | 71.25           | 22.87          | 0.24  |    | Hg | 3.72           | 4.29  | 4.81  | 14.98           | 72.2           | 22.58           | 64.60          | 7.60  |
| 5  | S  | 12.57          | 0.86  | 2.00 | 30.43           | 54.14          | 42.57           | 42.00          | 12.14 | 25 | S  | 0.89           | 4.46  | 10.71 | 10.06           | 73.88          | 18.75           | 65.19          | 8.69  |
|    | Hg | 2.74           | 4.08  | 8.64 | 31.64           | 52.90          | 43.22           | 41.32          | 11.58 |    | Hg | 0.35           | 4.20  | 10.26 | 17.51           | 67.68          | 22.61           | 62.58          | 5.10  |
| 6  | S  | 9.24           | 32.77 | 1.26 | 41.18           | 15.55          | 41.60           | 15.13          | 0.42  | 26 | S  | 6.06           | 1.01  | 7.07  | 23.08           | 62.78          | 29.29           | 56.57          | 6.21  |
|    | Hg | 3.09           | 30.80 | 0.64 | 49.98           | 15.49          | 50.23           | 15.24          | 0.25  |    | Hg | 4.32           | 2.17  | 6.57  | 17.90           | 69.04          | 28.03           | 58.91          | 10.13 |
| 7  | S  | 4.26           | 3.19  | 1.06 | 18.50           | 72.99          | 24.47           | 67.02          | 5.97  | 27 | S  | 2.67           | 2.22  | 4.89  | 29.19           | 61.03          | 33.33           | 56.89          | 4.14  |
|    | Hg | 2.55           | 1.33  | 0.83 | 25.90           | 69.39          | 29.16           | 66.13          | 3.26  |    | Hg | 2.08           | 3.27  | 1.24  | 3.59            | 89.82          | 8.62            | 84.79          | 5.03  |
| 8  | S  | 30.95          | 1.19  | 0.60 | 17.05           | 50.21          | 29.17           | 38.09          | 12.12 | 28 | S  | 3.56           | 3.56  | 3.11  | 7.17            | 82.6           | 19.11           | 70.66          | 11.94 |
|    | Hg | 5.20           | 5.09  | 7.92 | 26.12           | 55.67          | 39.05           | 42.74          | 12.93 |    | Hg | 0.66           | 1.57  | 1.56  | 11.76           | 84.45          | 21.20           | 75.01          | 9.44  |
| 9  | S  | 2.86           | 1.90  | 0.95 | 31.23           | 63.06          | 38.10           | 56.19          | 6.87  | 29 | S  | 2.04           | 2.86  | 1.63  | 12.21           | 81.26          | 23.67           | 69.8           | 11.46 |
|    | Hg | 6.36           | 1.16  | 0.44 | 32.87           | 59.17          | 37.38           | 54.66          | 4.51  |    | Hg | 1.07           | 0.60  | 1.26  | 13.85           | 83.22          | 27.06           | 70.01          | 13.21 |
| 10 | S  | 5.61           | 0.93  | 4.67 | 21.65           | 67.14          | 23.36           | 65.43          | 1.71  | 30 | S  | 1.61           | 0.69  | 8.06  | 0.88            | 88.76          | 10.60           | 79.04          | 9.72  |
|    | Hg | 1.32           | 7.75  | 1.26 | 21.09           | 68.58          | 23.19           | 66.48          | 2.10  |    | Hg | 1.51           | 0.86  | 3.91  | 3.58            | 90.14          | 12.13           | 81.59          | 8.55  |
| 11 | S  | 2.73           | 0.91  | 0.91 | 17.89           | 77.56          | 24.55           | 70.90          | 6.66  | 31 | S  | 1.04           | 0.62  | 7.45  | 5.56            | 85.33          | 8.70            | 82.19          | 3.14  |
|    | Hg | 4.13           | 0.40  | 1.04 | 12.06           | 82.37          | 17.10           | 77.33          | 5.04  |    | Hg | 1.51           | 1.19  | 6.99  | 2.15            | 88.16          | 8.26            | 82.05          | 6.11  |
| 12 | S  | 2.80           | 1.87  | 0.93 | 8.45            | 85.95          | 16.82           | 77.58          | 8.37  | 32 | S  | 29.89          | 5.43  | 4.89  | 26.91           | 32.88          | 27.17           | 32.62          | 0.26  |
|    | Hg | 2.68           | 1.34  | 4.88 | 8.23            | 82.87          | 19.11           | 71.99          | 10.88 |    | Hg | 14.10          | 10.18 | 7.34  | 28.02           | 40.36          | 28.49           | 39.89          | 0.47  |
| 13 | S  | 22.09          | 3.61  | 1.61 | 32.93           | 39.76          | 33.33           | 39.36          | 0.40  | 33 | S  | 1.30           | 1.30  | 2.60  | 25.98           | 68.82          | 33.77           | 61.03          | 7.79  |
|    | Hg | 18.64          | 3.45  | 2.49 | 33.77           | 41.65          | 34.42           | 41.00          | 0.65  |    | Hg | 1.01           | 1.86  | 5.45  | 25.20           | 66.48          | 30.94           | 60.74          | 5.74  |
| 14 | S  | 13.07          | 11.11 | 0.65 | 39.22           | 35.95          | 48.37           | 26.8           | 9.15  | 34 | S  | 6.49           | 2.60  | 2.60  | 9.10            | 79.21          | 14.29           | 74.02          | 5.19  |
|    | Hg | 4.13           | 5.45  | 0.17 | 54.51           | 35.74          | 60.73           | 29.52          | 6.22  |    | Hg | 7.54           | 2.39  | 2.52  | 7.91            | 79.64          | 14.69           | 72.86          | 6.78  |
| 15 | S  | 8.74           | 0.49  | 4.85 | 38.80           | 47.12          | 43.69           | 42.23          | 4.89  | 35 | S  | 48.28          | 0.86  | 3.88  | 25.67           | 21.31          | 27.59           | 19.39          | 1.92  |
|    | Hg | 1.11           | 0.86  | 4.86 | 42.44           | 50.73          | 49.99           | 43.18          | 7.55  |    | Hg | 5.71           | 0.69  | 0.57  | 47.65           | 45.38          | 49.33           | 43.70          | 1.68  |
| 16 | S  | 0.51           | 4.55  | 3.03 | 2.24            | 89.67          | 12.12           | 79.79          | 9.88  | 36 | S  | 0.00           | 1.98  | 1.98  | 34.76           | 61.28          | 36.63           | 59.41          | 1.87  |
|    | Hg | 1.15           | 5.13  | 4.91 | 0.38            | 88.43          | 12.09           | 76.72          | 11.71 |    | Hg | 0.06           | 1.65  | 1.67  | 35.89           | 60.73          | 37.71           | 58.91          | 1.82  |
| 17 | S  | 10.91          | 4.55  | 0.91 | 25.21           | 58.42          | 30.91           | 52.72          | 5.70  | 37 | S  | 5.32           | 2.48  | 2.84  | 7.52            | 81.84          | 10.28           | 79.08          | 2.76  |
|    | Hg | 6.06           | 1.31  | 8.34 | 25.42           | 58.87          | 32.28           | 52.01          | 6.86  |    | Hg | 5.07           | 2.54  | 2.11  | 9.06            | 81.22          | 12.55           | 77.73          | 3.49  |
| 18 | S  | 7.25           | 5.80  | 1.45 | 7.25            | 78.25          | 18.84           | 66.66          | 11.59 | 38 | S  | 5.05           | 1.81  | 4.69  | 4.57            | 83.88          | 12.64           | 75.81          | 8.07  |
|    | Hg | 2.93           | 5.78  | 0.43 | 11.51           | 79.35          | 16.48           | 74.38          | 4.97  |    | Hg | 5.33           | 3.97  | 6.64  | 7.82            | 76.24          | 14.34           | 69.72          | 6.52  |
| 19 | S  | 5.83           | 0.00  | 0.00 | 25.32           | 68.85          | 28.16           | 66.01          | 2.84  | 39 | S  | 9.52           | 3.17  | 1.59  | 19.05           | 66.67          | 22.22           | 63.50          | 3.17  |
|    | Hg | 3.18           | 1.61  | 1.57 | 26.87           | 66.77          | 29.05           | 64.59          | 2.18  |    | Hg | 7.02           | 5.56  | 5.14  | 20.88           | 61.40          | 22.07           | 60.21          | 1.19  |
| 20 | S  | 4.76           | 0.00  | 2.12 | 6.14            | 86.98          | 19.58           | 73.54          | 13.44 | 40 | S  | 9.73           | 0.88  | 1.77  | 42.53           | 45.09          | 47.79           | 39.83          | 5.26  |
|    | Hg | 0.89           | 0.67  | 3.71 | 7.37            | 87.36          | 19.69           | 75.04          | 12.32 |    | Hg | 7.30           | 0.93  | 5.19  | 45.04           | 41.54          | 49.21           | 37.37          | 4.17  |

注：<sup>a</sup>是 SCEPs-HNO<sub>3</sub>的结果；<sup>b</sup>是 SCEPs-PLTA 的结果；I 包含可交换态硫和可交换态汞；II 包含 HCl 可溶态硫和 HCl 可溶态汞；III 包含 HF 可溶态硫和 HF 可溶态汞；IV 包含硫化物硫和硫化物结合态汞；V 包含有机硫和有机结合态汞

化物硫和可交换态硫为主(三者占比之和超 80%)，5% 的煤以有机硫、硫化物硫和 HCl 可溶态硫为主。40 种煤中有 32.5% 的煤以有机结合态汞为主，5%

的煤以硫化物结合态汞为主，52.5% 的煤以有机结合态汞和硫化物结合态汞为主，2.5% 的煤以有机结合态汞、硫化物结合态汞和可交换态汞为主，

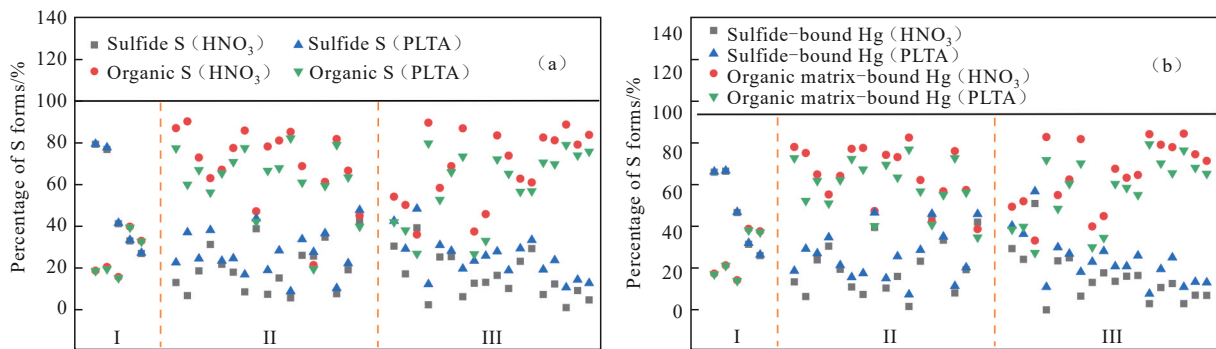


图5 HNO<sub>3</sub>浸提和PLTA测得煤中(a)有机硫、硫化物硫,(b)有机结合态汞和硫化物结合态汞含量  
Fig.5 Contents of (a) organic S, sulfide S, (b) organic matrix-bound Hg, and sulfide-bound Hg in coal measured by HNO<sub>3</sub> leaching and PLTA methods

表 5 SCEPs-HNO<sub>3</sub>和SCEPs-PLTA法测得不同粒径煤中形态硫和形态汞百分占比(%)  
Table 5 Percentages of different forms of sulfur and mercury in coal with different particle sizes measured by SCEPs-HNO<sub>3</sub> and SCEPs-PLTA methods (%)

| 煤样 | 元素 | 粒径小于 200 μm 煤样 |                |                |                | 差值    | 粒径小于 30 μm 煤样  |                |                |                | 差值   |
|----|----|----------------|----------------|----------------|----------------|-------|----------------|----------------|----------------|----------------|------|
|    |    | <sup>a</sup> Ⅳ | <sup>a</sup> V | <sup>b</sup> Ⅳ | <sup>b</sup> V |       | <sup>a</sup> Ⅳ | <sup>a</sup> V | <sup>b</sup> Ⅳ | <sup>b</sup> V |      |
| 8  | S  | 17.05          | 50.21          | 29.17          | 38.09          | 12.12 | 30.89          | 52.84          | 38.44          | 45.29          | 7.55 |
|    | Hg | 26.12          | 55.67          | 39.05          | 42.74          | 12.93 | 14.45          | 56.22          | 22.50          | 48.16          | 8.05 |
| 11 | S  | 17.89          | 77.56          | 24.55          | 70.90          | 6.66  | 20.11          | 66.40          | 23.00          | 63.51          | 2.89 |
|    | Hg | 12.06          | 82.37          | 17.10          | 77.33          | 5.04  | 15.33          | 64.54          | 16.53          | 63.35          | 1.19 |
| 12 | S  | 8.45           | 85.95          | 16.82          | 77.58          | 8.37  | 15.32          | 74.09          | 19.56          | 69.56          | 4.23 |
|    | Hg | 8.23           | 82.87          | 19.11          | 71.99          | 10.88 | 9.56           | 82.09          | 16.23          | 75.43          | 6.67 |
| 14 | S  | 39.22          | 35.95          | 48.37          | 26.8           | 9.15  | 41.39          | 32.33          | 46.49          | 27.23          | 5.10 |
|    | Hg | 54.51          | 35.74          | 60.73          | 29.52          | 6.22  | 47.25          | 28.02          | 22.64          | 65.02          | 2.23 |
| 16 | S  | 2.24           | 89.67          | 12.12          | 79.79          | 9.88  | 15.63          | 61.86          | 21.48          | 56.00          | 5.85 |
|    | Hg | 0.38           | 88.43          | 12.09          | 76.72          | 11.71 | 13.71          | 73.95          | 22.64          | 65.02          | 8.93 |
| 40 | S  | 42.53          | 45.09          | 47.79          | 39.83          | 5.26  | 41.28          | 43.77          | 42.74          | 42.31          | 1.46 |
|    | Hg | 45.04          | 41.54          | 49.21          | 37.37          | 4.17  | 32.21          | 51.06          | 33.29          | 49.97          | 1.08 |

注:<sup>a</sup>是SCEPs-HNO<sub>3</sub>的结果;<sup>b</sup>是SCEPs-PLTA的结果

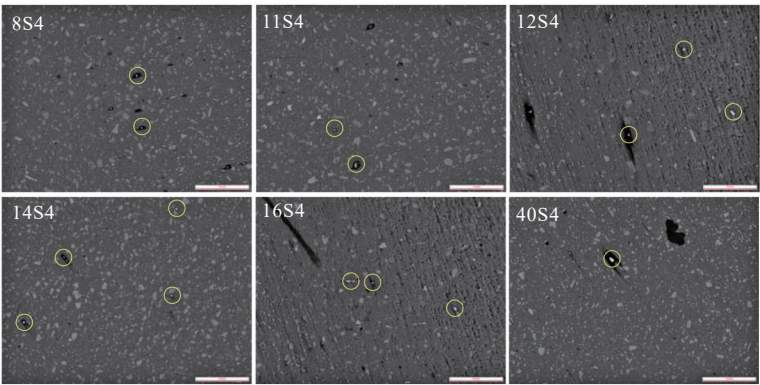


图 6 30 μm脱矿煤在OM下黄铁矿的微观赋存形态  
Fig.6 Microscopic occurrence forms of pyrite in 30 μm demineralized coal with OM

7.5%的煤以有机结合态汞、硫化物结合态汞和HCl可溶态汞为主。40种煤中主要为含有机硫和硫化物硫、有机结合态汞和硫化物结合态汞的煤,占比高于40%,其次为主要含有机硫和有机结合态汞的煤,占比高于30%。

2.4 煤中硫和汞的相关性分析

为了系统考察煤中硫和汞的相关性,下面对40种原煤中硫和汞含量、每种原煤及其预处理残渣中硫和汞含量、40种煤中相同赋存形态硫和汞含量以及40种煤中相同赋存形态硫和汞的百分占比进行

表 6 原煤和残渣中硫和汞的含量以及不同赋存形态硫和汞的含量

Table 6 Contents of sulfur and mercury in coals and residues, and the contents of their different occurrence forms

| 煤样 | 元素 | 预处理残渣中硫和汞含量 |        |        |        |        | 不同赋存形态硫和汞含量 |       |      |        |        | 煤样 | 元素 | 预处理残渣中硫和汞含量 |        |        |        |       | 不同赋存形态硫和汞含量 |       |       |        |       |
|----|----|-------------|--------|--------|--------|--------|-------------|-------|------|--------|--------|----|----|-------------|--------|--------|--------|-------|-------------|-------|-------|--------|-------|
|    |    | RC          | S1     | S2     | S3     | SP     | I           | Ⅱ     | Ⅲ    | Ⅳ      | V      |    |    | RC          | S1     | S2     | S3     | SP    | I           | Ⅱ     | Ⅲ     | Ⅳ      | V     |
| 1  | S  | 0.31        | 0.31   | 0.31   | 0.31   | 0.07   | 0.00        | 0.00  | 0.00 | 0.24   | 0.07   | 21 | S  | 2.44        | 1.50   | 1.44   | 1.22   | 0.57  | 0.94        | 0.06  | 0.22  | 0.65   | 0.57  |
|    | Hg | 72.80       | 72.23  | 71.85  | 71.33  | 14.80  | 0.57        | 0.38  | 0.52 | 56.53  | 14.8   |    | Hg | 176.50      | 174.37 | 111.21 | 101.04 | 43.94 | 2.13        | 63.16 | 10.17 | 57.10  | 43.94 |
| 2  | S  | 1.35        | 1.33   | 1.32   | 1.31   | 0.50   | 0.02        | 0.01  | 0.01 | 0.81   | 0.5    | 22 | S  | 0.53        | 0.53   | 0.53   | 0.51   | 0.15  | 0.00        | 0.00  | 0.02  | 0.36   | 0.15  |
|    | Hg | 115.40      | 108.97 | 105.38 | 100.94 | 36.39  | 6.43        | 3.59  | 4.44 | 64.55  | 36.39  |    | Hg | 159.40      | 158.20 | 157.49 | 152.37 | 44.18 | 1.20        | 0.71  | 5.12  | 108.19 | 44.18 |
| 3  | S  | 2.00        | 1.98   | 1.97   | 1.96   | 1.59   | 0.02        | 0.01  | 0.01 | 0.37   | 1.59   | 23 | S  | 2.21        | 1.48   | 1.39   | 1.30   | 0.57  | 0.73        | 0.09  | 0.09  | 0.73   | 0.57  |
|    | Hg | 318.50      | 315.73 | 290.39 | 284.57 | 225.45 | 2.77        | 25.34 | 5.82 | 59.12  | 225.45 |    | Hg | 172.00      | 143.75 | 120.30 | 115.96 | 52.15 | 28.25       | 23.45 | 4.34  | 63.81  | 52.15 |
| 4  | S  | 1.85        | 1.81   | 1.80   | 1.80   | 1.44   | 0.04        | 0.01  | 0.00 | 0.36   | 1.44   | 24 | S  | 0.61        | 0.61   | 0.61   | 0.61   | 0.17  | 0.00        | 0.00  | 0.00  | 0.44   | 0.17  |
|    | Hg | 289.40      | 284.13 | 279.83 | 272.40 | 206.21 | 5.27        | 4.30  | 7.43 | 66.19  | 206.21 |    | Hg | 156.10      | 150.30 | 143.60 | 136.09 | 35.25 | 5.80        | 6.70  | 7.51  | 100.84 | 35.25 |
| 5  | S  | 3.50        | 3.06   | 3.03   | 2.96   | 1.49   | 0.44        | 0.03  | 0.07 | 1.47   | 1.49   | 25 | S  | 1.12        | 1.11   | 1.06   | 0.94   | 0.21  | 0.01        | 0.05  | 0.12  | 0.73   | 0.21  |
|    | Hg | 85.30       | 82.96  | 79.48  | 72.11  | 36.87  | 2.34        | 3.48  | 7.37 | 35.24  | 36.87  |    | Hg | 184.00      | 183.36 | 175.63 | 156.75 | 41.61 | 0.64        | 7.73  | 18.88 | 115.14 | 41.61 |
| 6  | S  | 2.38        | 2.16   | 1.38   | 1.35   | 0.99   | 0.22        | 0.78  | 0.03 | 0.36   | 0.99   | 26 | S  | 0.99        | 0.93   | 0.92   | 0.85   | 0.29  | 0.06        | 0.01  | 0.07  | 0.56   | 0.29  |
|    | Hg | 155.50      | 150.70 | 102.80 | 101.80 | 78.10  | 4.80        | 47.90 | 1.00 | 23.70  | 78.1   |    | Hg | 56.30       | 53.87  | 52.65  | 48.95  | 15.78 | 2.43        | 1.22  | 3.70  | 33.17  | 15.78 |
| 7  | S  | 0.94        | 0.90   | 0.87   | 0.86   | 0.23   | 0.04        | 0.03  | 0.01 | 0.63   | 0.23   | 27 | S  | 2.25        | 2.19   | 2.14   | 2.03   | 0.75  | 0.06        | 0.05  | 0.11  | 1.28   | 0.75  |
|    | Hg | 88.00       | 85.76  | 84.59  | 83.86  | 25.66  | 2.24        | 1.17  | 0.73 | 58.20  | 25.66  |    | Hg | 75.90       | 74.32  | 71.84  | 70.90  | 6.54  | 1.58        | 2.48  | 0.94  | 64.36  | 6.54  |
| 8  | S  | 1.68        | 1.16   | 1.14   | 1.13   | 0.49   | 0.52        | 0.02  | 0.01 | 0.64   | 0.49   | 28 | S  | 2.25        | 2.17   | 2.09   | 2.02   | 0.43  | 0.08        | 0.08  | 0.07  | 1.59   | 0.43  |
|    | Hg | 88.40       | 83.80  | 79.30  | 72.30  | 34.52  | 4.60        | 4.50  | 7.00 | 37.78  | 34.52  |    | Hg | 107.50      | 106.79 | 105.10 | 103.42 | 22.79 | 0.71        | 1.69  | 1.68  | 80.63  | 22.79 |
| 9  | S  | 1.05        | 1.02   | 1.00   | 0.99   | 0.40   | 0.03        | 0.02  | 0.01 | 0.59   | 0.4    | 29 | S  | 2.45        | 2.40   | 2.33   | 2.29   | 0.58  | 0.05        | 0.07  | 0.04  | 1.71   | 0.58  |
|    | Hg | 106.00      | 99.26  | 98.03  | 97.56  | 39.62  | 6.74        | 1.23  | 0.47 | 57.94  | 39.62  |    | Hg | 103.10      | 102.0  | 101.38 | 100.08 | 27.90 | 1.10        | 0.62  | 1.30  | 72.18  | 27.9  |
| 10 | S  | 1.07        | 1.01   | 1.00   | 0.95   | 0.25   | 0.06        | 0.01  | 0.05 | 0.70   | 0.25   | 30 | S  | 4.34        | 4.27   | 4.24   | 3.89   | 0.46  | 0.07        | 0.03  | 0.35  | 3.43   | 0.46  |
|    | Hg | 90.70       | 89.50  | 82.47  | 81.33  | 21.03  | 1.20        | 7.03  | 1.14 | 60.30  | 21.03  |    | Hg | 100.70      | 99.18  | 98.31  | 94.37  | 12.21 | 1.52        | 0.87  | 3.94  | 82.16  | 12.21 |
| 11 | S  | 1.10        | 1.07   | 1.06   | 1.05   | 0.27   | 0.03        | 0.01  | 0.01 | 0.78   | 0.27   | 31 | S  | 4.83        | 4.78   | 4.75   | 4.39   | 0.42  | 0.05        | 0.03  | 0.36  | 3.97   | 0.42  |
|    | Hg | 54.90       | 52.63  | 52.41  | 51.84  | 9.39   | 2.27        | 0.22  | 0.57 | 42.45  | 9.39   |    | Hg | 102.00      | 100.46 | 99.25  | 92.12  | 8.43  | 1.54        | 1.21  | 7.13  | 83.69  | 8.43  |
| 12 | S  | 1.07        | 1.04   | 1.02   | 1.01   | 0.18   | 0.03        | 0.02  | 0.01 | 0.83   | 0.18   | 32 | S  | 1.84        | 1.29   | 1.19   | 1.10   | 0.50  | 0.55        | 0.10  | 0.09  | 0.60   | 0.5   |
|    | Hg | 55.30       | 53.82  | 53.08  | 50.38  | 10.57  | 1.48        | 0.74  | 2.70 | 39.81  | 10.57  |    | Hg | 56.40       | 48.45  | 42.71  | 38.57  | 16.07 | 7.95        | 5.74  | 4.14  | 22.50  | 16.07 |
| 13 | S  | 2.49        | 1.94   | 1.85   | 1.81   | 0.83   | 0.55        | 0.09  | 0.04 | 0.98   | 0.83   | 33 | S  | 0.77        | 0.76   | 0.75   | 0.73   | 0.26  | 0.01        | 0.01  | 0.02  | 0.47   | 0.26  |
|    | Hg | 120.80      | 98.28  | 94.11  | 91.10  | 41.58  | 22.52       | 4.17  | 3.01 | 49.52  | 41.58  |    | Hg | 164.90      | 163.24 | 160.17 | 151.19 | 51.02 | 1.66        | 3.07  | 8.98  | 100.17 | 51.02 |
| 14 | S  | 1.53        | 1.33   | 1.16   | 1.15   | 0.74   | 0.20        | 0.17  | 0.01 | 0.41   | 0.74   | 34 | S  | 0.77        | 0.72   | 0.70   | 0.68   | 0.11  | 0.05        | 0.02  | 0.02  | 0.57   | 0.11  |
|    | Hg | 60.6        | 58.1   | 54.8   | 54.7   | 36.8   | 2.50        | 3.30  | 0.10 | 17.90  | 36.8   |    | Hg | 62.30       | 57.60  | 56.11  | 54.54  | 9.15  | 4.70        | 1.49  | 1.57  | 45.39  | 9.15  |
| 15 | S  | 2.06        | 1.88   | 1.87   | 1.77   | 0.90   | 0.18        | 0.01  | 0.10 | 0.87   | 0.9    | 35 | S  | 2.32        | 1.20   | 1.18   | 1.09   | 0.64  | 1.12        | 0.02  | 0.09  | 0.45   | 0.64  |
|    | Hg | 91.80       | 90.78  | 89.99  | 85.53  | 45.89  | 1.02        | 0.79  | 4.46 | 39.64  | 45.89  |    | Hg | 125.30      | 118.14 | 117.27 | 116.56 | 61.81 | 7.16        | 0.87  | 0.71  | 54.75  | 61.81 |
| 16 | S  | 1.98        | 1.97   | 1.88   | 1.82   | 0.24   | 0.01        | 0.09  | 0.06 | 1.58   | 0.24   | 36 | S  | 1.01        | 1.01   | 0.99   | 0.97   | 0.37  | 0.00        | 0.02  | 0.02  | 0.60   | 0.37  |
|    | Hg | 170.30      | 168.35 | 159.62 | 151.26 | 20.59  | 1.95        | 8.73  | 8.36 | 130.67 | 20.59  |    | Hg | 48.00       | 47.97  | 47.18  | 46.38  | 18.10 | 0.03        | 0.79  | 0.80  | 28.28  | 18.1  |
| 17 | S  | 1.10        | 0.98   | 0.93   | 0.92   | 0.34   | 0.12        | 0.05  | 0.01 | 0.58   | 0.34   | 37 | S  | 2.82        | 2.67   | 2.60   | 2.52   | 0.29  | 0.15        | 0.07  | 0.08  | 2.23   | 0.29  |
|    | Hg | 107.80      | 101.27 | 99.86  | 90.87  | 34.80  | 6.53        | 1.41  | 8.99 | 56.07  | 34.8   |    | Hg | 63.10       | 59.90  | 58.30  | 56.97  | 7.92  | 3.20        | 1.60  | 1.33  | 49.05  | 7.92  |
| 18 | S  | 0.69        | 0.64   | 0.60   | 0.59   | 0.13   | 0.05        | 0.04  | 0.01 | 0.46   | 0.13   | 38 | S  | 2.77        | 2.63   | 2.58   | 2.45   | 0.35  | 0.14        | 0.05  | 0.13  | 2.10   | 0.35  |
|    | Hg | 115.90      | 112.50 | 105.80 | 105.30 | 19.10  | 3.40        | 6.70  | 0.50 | 86.20  | 19.1   |    | Hg | 54.20       | 51.31  | 49.16  | 45.56  | 7.77  | 2.89        | 2.15  | 3.60  | 37.79  | 7.77  |
| 19 | S  | 1.03        | 0.97   | 0.97   | 0.97   | 0.29   | 0.06        | 0.00  | 0.00 | 0.68   | 0.29   | 39 | S  | 0.63        | 0.57   | 0.55   | 0.54   | 0.14  | 0.06        | 0.02  | 0.01  | 0.40   | 0.14  |
|    | Hg | 44.00       | 42.60  | 41.89  | 41.20  | 12.78  | 1.40        | 0.71  | 0.69 | 28.42  | 12.78  |    | Hg | 70.20       | 65.27  | 61.37  | 57.76  | 15.49 | 4.93        | 3.90  | 3.61  | 42.27  | 15.49 |
| 20 | S  | 1.89        | 1.80   | 1.80   | 1.76   | 0.37   | 0.09        | 0.00  | 0.04 | 1.39   | 0.37   | 40 | S  | 1.13        | 1.02   | 1.01   | 0.99   | 0.54  | 0.11        | 0.01  | 0.02  | 0.45   | 0.54  |
|    | Hg | 55.30       | 54.81  | 54.44  | 52.39  | 10.89  | 0.49        | 0.37  | 2.05 | 41.50  | 10.89  |    | Hg | 126.90      | 117.63 | 116.45 | 109.86 | 62.45 | 9.27        | 1.18  | 6.59  | 47.41  | 62.45 |

注:硫含量为质量分数,%;汞含量的单位为 ng/g;I包含可交换态硫和可交换态汞;Ⅱ包含 HCl 可溶态硫和 HCl 可溶态汞;Ⅲ包含 HF 可溶态硫和 HF 可溶态汞;Ⅳ包含有机硫和有机结合态汞;V 包含硫化物硫和硫化物结合态汞

了相关性分析,结果如图 7 所示。分析可知,40 种原煤中硫和汞含量间无相关性,而每种原煤及其预处理残渣中硫和汞含量间具有显著的正相关性,相关指数为 0.692 8~0.999 9,见表 7。此外,40 种煤中相同赋存形态硫和汞含量间无相关性,而 40 种煤中相同赋存形态硫和汞含量的百分占比间具有相关

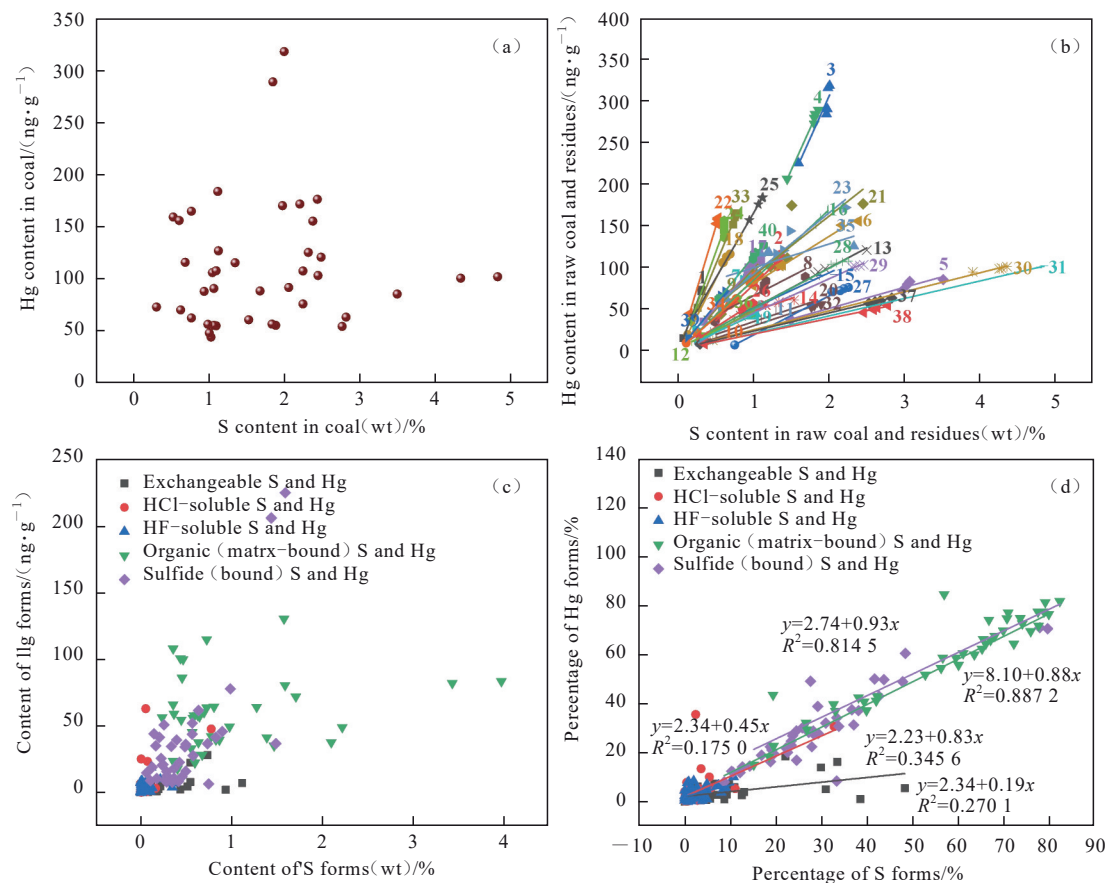


图 7 (a)40 种原煤中硫和汞含量间的相关性;(b)每种原煤及其预处理残渣中硫和汞含量的相关性;(c)40 种煤相同赋存形态硫和汞含量间的相关性;(d)40 种煤中相同赋存形态硫和汞含量百分占比间的相关性

Fig.7 (a) Correlations between sulfur and mercury contents in 40 kinds of raw coals; (b) Correlations between sulfur and mercury contents in each kind of raw coal and its pre-treated residue; (c) Correlations between sulfur and mercury contents in the same occurrence forms of 40 kinds of coals; (d) Correlations between the percentage contents of sulfur and mercury in the same occurrence forms of 40 kinds of coals

性,且有机硫和有机结合态汞、硫化物硫和硫化物结合态汞间具有显著的正相关性,相关指数分别为 0.887 2 和 0.814 5。硫化物硫和硫化物结合态汞间的显著正相关性是源于汞与黄铁矿之间的强伴生关系<sup>[21-26]</sup>,且主要以 Hg 取代 FeS<sub>2</sub> 晶胞中的 S<sub>2</sub><sup>2-</sup> 的固溶体形式伴生<sup>[45]</sup>。而煤中非黄铁矿汞含量可能与有机硫含量相关<sup>[27]</sup>。汞与腐殖质中的还原性硫官

能团(比如硫醇(RSH)、二硫(R—SS—R)和二硫酮(R—SSH)具有非常高的亲和力<sup>[46]</sup>。煤中有机硫与有机结合态汞之间的显著正相关性可能反映了煤中有机硫化合物对汞的亲合力<sup>[47]</sup>。40 种煤中可交换态硫和可交换态汞、HCl 可溶态硫和 HCl 可溶态汞、HF 可溶态硫和 HF 可溶态汞含量百分占比间相关性不显著,相关指数分别为 0.270 1、0.345 6 和 0.175 0。

| 表 7 每种原煤及其预处理残渣中硫和汞含量间的相关性系数(R <sup>2</sup> )                                                                                      |         |         |         |         |         |         |         |         |         |         |
|------------------------------------------------------------------------------------------------------------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Table 7 Correlation coefficient (R <sup>2</sup> ) between sulfur and mercury content in each raw coal and its pretreatment residue |         |         |         |         |         |         |         |         |         |         |
| 煤样                                                                                                                                 | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       | 10      |
| R <sup>2</sup>                                                                                                                     | 0.999 4 | 0.979 4 | 0.854 5 | 0.985 0 | 0.952 0 | 0.989 6 | 0.997 1 | 0.786 6 | 0.996 4 | 0.992 4 |
| 煤样                                                                                                                                 | 11      | 12      | 13      | 14      | 15      | 16      | 17      | 18      | 19      | 20      |
| R <sup>2</sup>                                                                                                                     | 0.999 8 | 0.997 2 | 0.994 3 | 0.886 3 | 0.972 8 | 0.998 6 | 0.980 1 | 0.993 5 | 0.997 9 | 0.997 4 |
| 煤样                                                                                                                                 | 21      | 22      | 23      | 24      | 25      | 26      | 27      | 28      | 29      | 30      |
| R <sup>2</sup>                                                                                                                     | 0.776 9 | 0.999 8 | 0.928 6 | 0.970 6 | 0.999 9 | 0.999 2 | 0.993 7 | 0.993 2 | 0.997 2 | 0.997 3 |
| 煤样                                                                                                                                 | 31      | 32      | 33      | 34      | 35      | 36      | 37      | 38      | 39      | 40      |
| R <sup>2</sup>                                                                                                                     | 0.999 9 | 0.918 5 | 0.997 4 | 0.999 8 | 0.692 8 | 0.999 9 | 0.999 9 | 0.996 0 | 0.994 0 | 0.992 6 |

3 结语

本文采用 SCEPs-HNO<sub>3</sub> 和 SCEPs-PLTA 法将

40 种煤中的硫和汞同步分为可交换态、HCl 可溶态、HF 可溶态、硫化物(结合)态和有机(结合)态 5 种赋存形态。定量分析了煤样粒径对 SCEPs-

PLTA 和 SCEPs-HNO<sub>3</sub> 法同步分析煤中硫和汞赋存形态间偏差的影响,并系统分析了煤中硫和汞含量间的相关性。研究得出以下结论:

1)40 种煤中含细粒黄铁矿的煤占比高达 87.5%。对于主要含粗粒黄铁矿的煤, SCEPs-PLTA 与 SCEPs-HNO<sub>3</sub> 法检测结果偏差小于 1%。2 号煤因硫含量高且主要含细粒黄铁矿,两种方法检测结果偏差较大,约 30%。其余煤采用两种方法检测结果偏差在 1%~15%。两种方法的分析偏差取决于煤中细粒黄铁矿的含量以及细粒黄铁矿中伴生的汞含量。将煤样粒径减小至小于 30 μm 会将 SCEPs-PLTA 和 SCEPs-HNO<sub>3</sub> 法间的偏差降低 3%~5%,但 HNO<sub>3</sub> 无法完全浸提煤中的细粒黄铁矿。

2)40 种煤中主要为含有机硫和硫化物硫、有机

结合态汞和硫化物结合态汞的煤,占比高于 40%,其次为主要含有机硫和有机结合态汞的煤,占比高于 30%。

3)40 种原煤中硫和汞含量间无相关性,每种原煤及其 SCEPs-PLTA 预处理残渣中硫和汞含量间具有显著的正相关性,相关系数为 0.692 8~0.999 9。40 种煤中相同赋存形态硫和汞含量间无相关性,而相同赋存形态硫和汞含量百分占比间具有相关性,且有机硫和有机结合态汞、硫化物硫和硫化物结合态汞间具有显著的正相关性,相关指数分别为 0.887 2 和 0.814 5。可交换态硫和可交换态汞、HCl 可溶态硫和 HCl 可溶态汞、HF 可溶态硫和 HF 可溶态汞间相关性不显著。

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